

Supplementary Materials

Solvent and H/D Isotopic Substitution Effects on the Krichevskii Parameter of Solutes

A Novel approach to their accurate determination

by

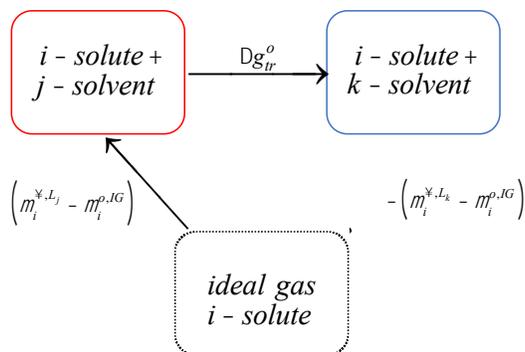
Ariel A. Chialvo and Oscar D. Crisalle

SI-1: Alternatives solvation cycle paths for the study of the transfer Gibbs free energy of an infinitely dilute solute

We can also portray the alluded thought experiment, this time involving a three-step solvation cycle-path for a single i - solute species, according to either the scheme of Figure SI-1 in terms of $\Delta m_i^{\infty, L, a} \equiv m_i^{\infty, L, a} - m_i^{\rho, IG}$ or Figure SI-2 in terms of Ben-Naim's solvation quantities.

[1]

Figure SI-1



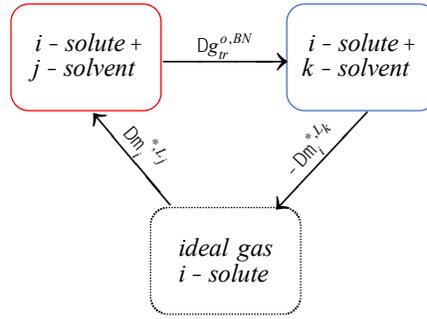
For the first case, Figure SI-1 indicates that $\Delta g_{tr}^o - (m_i^{\infty, L_k} - m_i^{\rho, IG}) + (m_i^{\infty, L_j} - m_i^{\rho, IG}) = 0$ so

that

$$\begin{aligned}
\Delta g_{tr}^o(T, P) &= \left(\mu_i^{\infty, L_k} - \mu_i^{\infty, L_j} \right) \\
&= kT \ln \left(\hat{\phi}_i^{\infty, L_k} / \hat{\phi}_i^{\infty, L_j} \right) \\
&= kT \ln \left(\mathcal{H}_{i,k}^{IS} / \mathcal{H}_{i,j}^{IS} \right)
\end{aligned} \tag{SI-1.1}$$

where $\mathcal{H}_{i,\alpha}^{IS}(T, P)$ and $\hat{f}_i^{*,L,\alpha}(T, P)$ define Henry's law constant and corresponding fugacity coefficient in the liquid phase for the i - solute in the α - solvent environment, respectively.

Figure SI-2



For the second case, the cycle in Figure SI-2 suggests that $Dg_{tr}^{o,BN} + Dm_i^{*,L,j} - Dm_i^{*,L,k} = 0$, where the superscript BN denotes Ben-Naim's solute transfer definition, [2] *i.e.*,

$$\begin{aligned}
\Delta g_{tr}^{o,BN}(T, P) &= \Delta \mu_i^{*,\infty,L_k} - \Delta \mu_i^{*,\infty,L_j} \\
&= \mu_i^{r,\infty,L_k}(T, \rho_k^o) - \mu_i^{r,\infty,L_j}(T, \rho_j^o) \\
&= kT \left[\ln \left(\hat{\phi}_i^{\infty} z_k^o \right)_{TP} - \ln \left(\hat{\phi}_i^{\infty} z_j^o \right)_{TP} \right] \\
&= kT \left[\ln \left(\mathcal{H}_{i,k}^{IS} / \mathcal{H}_{i,j}^{IS} \right) - \ln \left(\rho_k^o / \rho_j^o \right) \right] \\
&\cong kT \left[\ln \left(\hat{\phi}_i^{\infty} z_k^o \right)_{TP_k,\sigma} - \ln \left(\hat{\phi}_i^{\infty} z_j^o \right)_{TP_j,\sigma} \right] \\
&= kT \left[\ln \left(\hat{\phi}_i^{\infty} / \rho_k^o \right)_{TP_k,\sigma} - \ln \left(\hat{\phi}_i^{\infty} / \rho_j^o \right)_{TP_j,\sigma} \right]
\end{aligned} \tag{SI-1.2}$$

Thus, from Eqns. SI-1.1 and SI-1.2, we find that $Dg_{tr}^{o,BN}(T, P) @ Dg_{tr}^o(T, P) - kT \ln \left(r_k^o / r_j^o \right)$, where @ highlights the fact that we assume a negligible pressure effect of the properties for the change $P \rightarrow P_s(T)$.

SI-2: Determination of the standard Gibbs free energy of hydration of hydrogen isotopes in light and/or heavy water

Here we calculate $D_h G_{D_2,(H_2O)}^\infty(T, P_o)$ from experimental data of $D_{tr} G_{(D_2)}^*(T, P_o)$, and $D_h G_{H_2,(D_2O)}^\infty(T, P_o)$ from experimental data of $D_{tr} G_{(H_2)}^*(T, P_o)$, complemented with those for $r_{H_2O}^o$ and $r_{D_2O}^o$. For that purpose, we invoke the accurate data in Table VIII of Scharlin & Battino [3] for $D_{tr} G_{(D_2)}^*(T, P_o)$ and $D_{tr} G_{(H_2)}^*(T, P_o)$, as well as the corresponding solubilities in heavy water from their Table III. Then, from A11 we calculate,

$$\begin{aligned} D_h G_{D_2,(D_2O)}^\infty(T, P_o) &= -kT \ln(x_{D_2}/m_{D_2}^o MW_{D_2O}) \\ &= -298 \times 8.314 \times 10^{-3} \ln(1.919 \times 10^{-5} \times 49.9) \\ &= 17.222 \text{ kJ/mol} \end{aligned}$$

Moreover, from Eqns. (12)-(13) and Table VIII of Scharlin & Battino [3], we find

$$\begin{aligned} D_h G_{D_2,(H_2O)}^\infty(T, P_o) &= D_h G_{D_2,(D_2O)}^\infty - D_{tr} G_{(D_2)}^* - kT \ln(r_{D_2O}^o/r_{H_2O}^o) \\ &\quad - kT \ln(MW_{D_2O}/MW_{H_2O}) \\ &= 17.222 + 0.597 - 298 \times 8.314 \times 10^{-3} \times [\ln(0.05514 \times 20.027) - \\ &\quad \ln(0.05532 \times 18.020)] \\ &= 17.565 \text{ kJ/mol} \end{aligned}$$

By the same procedure, and invoking $D_h G_{H_2,(H_2O)}^\infty = 17.687 \text{ kJ/mol}$ from Ref. [4], we find that

$$\begin{aligned} D_h G_{H_2,(D_2O)}^\infty(T, P_o) &= D_h G_{H_2,(H_2O)}^\infty + D_{tr} G_{(H_2)}^* + kT \ln(r_{D_2O}^o/r_{H_2O}^o) \\ &\quad + kT \ln(MW_{D_2O}/MW_{H_2O}) \\ &= 17.687 - 0.546 + 298 \times 8.314 \times 10^{-3} \times [\ln(0.05514 \times 20.027) - \\ &\quad \ln(0.05532 \times 18.020)] \\ &= 17.394 \text{ kJ/mol} \end{aligned}$$

References:

- [1] A. Ben-Naim, Solvation Thermodynamics, Plenum Press, New York, 1987.
- [2] A. Ben-Naim, Y. Marcus, Solvation Thermodynamics Of Nonionic Solutes, J. Chem. Phys., 81 (1984) 2016-2027.
- [3] P. Scharlin, R. Battino, Solubility of 13 Nonpolar Gases in Deuterium-Oxide at 15-Degrees-C-45-Degrees-C and 101.325-Kpa - Thermodynamics of Transfer of Nonpolar Gases from H₂O to D₂O, J. Solution Chem., 21 (1992) 67-91.
- [4] R. Fernandez-Prini, J.L. Alvarez, A.H. Harvey, Henry's constants and vapor-liquid distribution constants for gaseous solutes in H₂O and D₂O at high temperatures, J. Phys. Chem. Ref. Data, 32 (2003) 903-916.